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# Composition of Uranium Oxide Surface Layers Analyzed by m-Raman Spectroscopy

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November 25, 2003

MRS 2003 Fall Meeting  
Boston, MA, United States  
December 1, 2003 through December 5, 2003

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## Composition of uranium oxide surface layers analyzed by $\mu$ -Raman Spectroscopy.

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### Abstract.

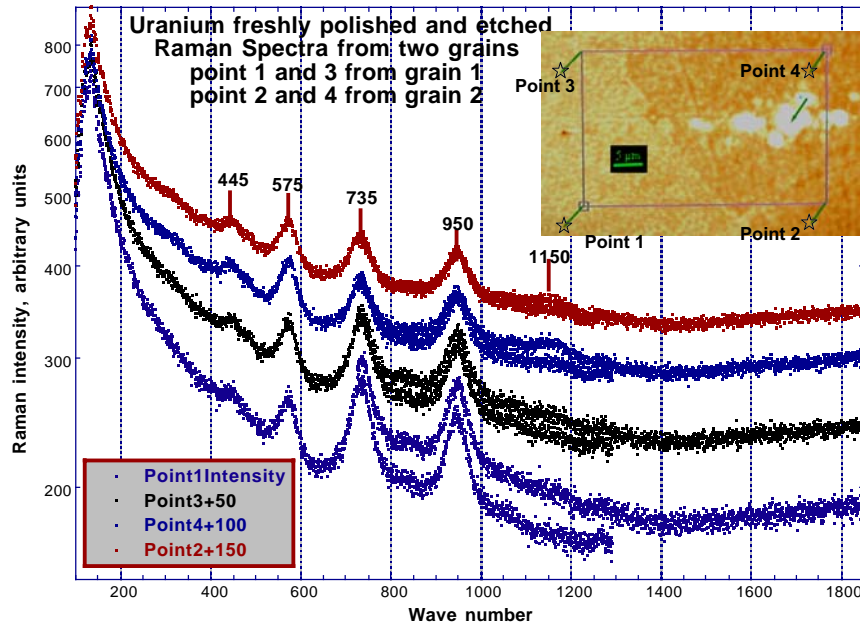
Oxide thickness and composition averaged over a few square millimeter has been measured with nm thickness resolution by diffuse reflectance fourier transform infrared (FTIR) spectroscopy<sup>1</sup>.  $\mu$ -Raman spectroscopy has been done on powders and bulk samples<sup>2</sup> in the past, and can now be done on surfaces layers with  $\mu$ m lateral and depth resolution using con-focal microscopy<sup>3</sup>. Here we apply con-focal-microscopy-based  $\mu$  - Raman spectroscopy to a freshly polished/lightly oxidized and to heavily oxidized uranium to determine its sensitivity. The spectra show that  $\mu$ -Raman spectroscopy does detect oxide thickness and oxide composition with high sensitivity.

### Experimental Results.

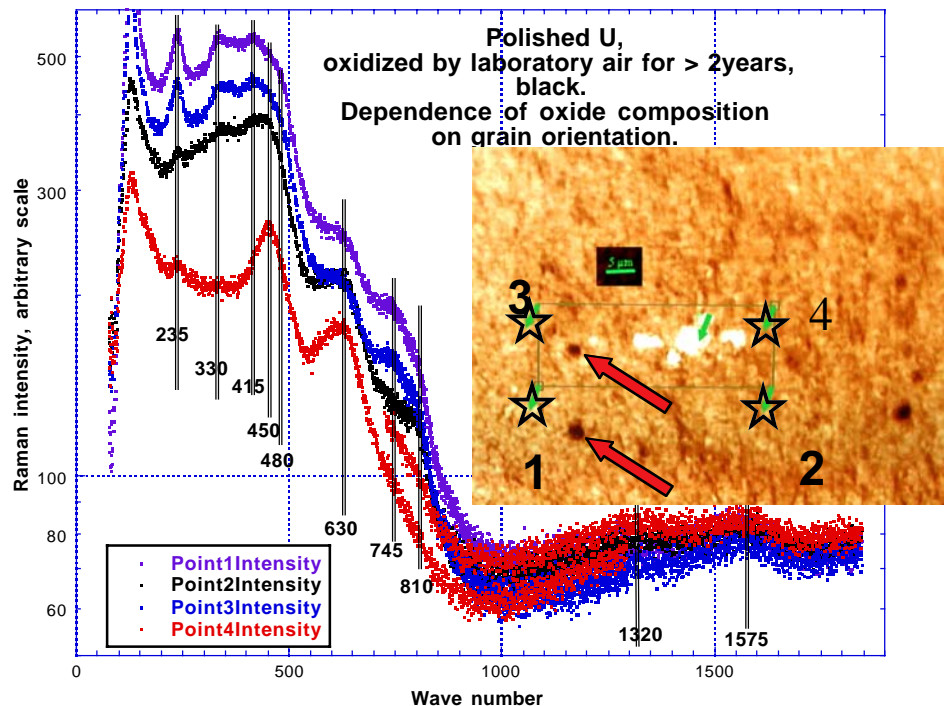
Freshly polished and etched uranium: Raman spectra were taken from two surface grains of a freshly polished and etched uranium surface. A commercial instrument (see reference 3), with a X50 objective was used. Results are shown in figure 1. The insert in figure 1 shows the two grains and the 4 analysis points: point 2 and 4 on the “darker” grain, points 1 and 3 on the lighter grain. 10 spectra of 30 seconds each were accumulated at each of the 4 analysis points. Peaks at 445 and 1150 wave numbers are associated with  $\text{UO}_2$ . The peak at  $\sim 575$  has been seen on  $\text{Kr}^+$  ion implanted  $\text{UO}_2$ , and has been attributed to vibrational modes of an imperfect urania lattice (see reference 2 and table 1). Points 2 and 4, both inside the darker grain, show a noticeable peak at 1150 and a peak at 445 slightly stronger than 1 and 3's, indicating that this grain's oxide layer is thicker. Bullock et al.<sup>4</sup> used electron microscopy-based spectroscopy and found that the rate of oxidation depends on the crystal orientation. These Raman spectra confirm this observation. Most importantly, the nm-scale oxide layers (hours after polishing and etching) are detectable on both grains by  $\mu$ -Raman spectroscopy.

Highly air-oxidized uranium: A polished surface of uranium, oxidized for more than 2 years, still shows distinctive grains (see insert in figure 2). The Raman spectra in figure 2 were taken at the 4 points shown in the insert, points 2 and 4 inside the slightly darker grain, points 1 and 3 outside that grain. The laser power was attenuated by a .3 density filter for these spectra. The two red arrows point to the spots where the un-attenuated laser spend 10x30 seconds and “burned” uranium oxide. The same square pattern shown in the insert was used, just shifted. It is surprising that the same laser fluence does *not* affect the darker grain. (The dark spots along the lower right hand edge are natural in-homogeneities.) The “burn” holes demonstrate a danger inherent in  $\mu$  - Raman spectroscopy, i.e. the highly focused laser beam has sufficient power to induce changes in the material under investigation. The papers cited in reference 2 also show this problem. The Raman spectra exhibit a great number of peaks, the general shape being

similar to that of the  $\text{U}_3\text{O}_8$  spectra in ref. 2 (all peak positions shaded in table 1), but not all of the peak positions agree. Spectrum 4, from inside the “grain”, is distinctly different from spectra 1 and 3 outside the “grain”, while spectrum 2 from inside the grain, is similar to spectra 1 and 3. Both facts substantiate that  $\mu$ -Raman reveals the local variability in uranium oxide composition.



**Fig. 1. Raman spectra from two uranium grains on a freshly polished and etched surface. Point 2 is the uppermost spectrum, followed by Point 4, Point 3, Point 1.**



**Figure 2. Raman spectra of 2 grains of a highly oxidized uranium surface.; Point 1 is the uppermost spectrum, followed by Point 2, Point 3 and Point 4.**

Species	Peak position, cm <sup>-1</sup>													
$\alpha$ U <sub>3</sub> O <sub>8</sub>		235	340	410			475		640		750	805		
U <sub>4</sub> O <sub>9</sub>	210					465								
UO <sub>2</sub>					446									1150
UO <sub>2</sub> +Kr ion					446			575						1150
$\beta$ - U <sub>3</sub> O <sub>7</sub>	210					465								
light oxide, Pt .2&4					446			575		735			950	1150
U+light oxide, Pt. 1&3					446			575		735			950	1150
heavy oxide,Pt 4		235			450				630		745	810		1320 1575
heavy oxide,Pt s. 1,2,3		235	330	415	450		480		630		745	810		1320 1575

**Table 1. Literature Raman lines (shaded) and lines observed on oxidized U surfaces.**

**Conclusion.** The Raman spectra of lightly and heavily oxidized uranium surfaces show that  $\mu$ -Raman spectroscopy can be used to determine local variations in surface oxide moiety, and the dependence of oxide thickness on the orientation of the underlying uranium grain. Oxide spectra are detectable within hours after polishing, when the oxide thickness is in the nm range.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

## References

<sup>1</sup> The study of the oxidation of uranium by external and diffuse reflectance FTIR spectroscopy using remote sensing and evacuable cell techniques, G.L. Powell et al., 9<sup>th</sup> Int. Conf. On Fourier Transform Spectroscopy, Calgary, Alberta, Canada, Aug. 23-27, 1993.

<sup>2</sup> Characterisation of uranium oxides by micro-Raman spectroscopy. Allen, GC Butler, IS Nguyen, AT. Journal of Nuclear Materials 144 (1987). 17-19. Raman Microprobe spectroscopy of Uranium Dioxide single crystals and ion implanted polycrystals. Graves, PR, Applied Spectroscopy, 44, 10, 1990, 1665-1667.

<sup>3</sup> Jobin Yvon, HORIBA, [www.jyhoriba.com](http://www.jyhoriba.com)

<sup>4</sup> Bullock, J.S. et al. Report Y/DZ-2358, Nov. 27, 2001